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<b>2003-610325/58</b> <b>A23 F01</b> <b>RHOD 2001.12.17</b> <b>RHODIANYL SNC</b> 2001.12.17 2001-016322(+2001FR-016322) (2003.06.20) C08L 77/06, C08G 69/06, C08J 5/18 (C08L 77/06, 77:00) <b>Thermoplastic polymer composition, used e.g. for production of moulded products, film or fibres, contains a functionalised, hyper-branched copolyamide as rheology modifier</b> <b>C2003-166585</b>	<b>A(5-F1B2, 8-M6, 11-B1) F(1-D)</b>  A, A', A = reactive polymer-forming groups; B, B', B = polymer-forming groups which react with A, A' or A; R, R' = hydrocarbon units, optionally with hetero-atoms; f = at least 2, preferably 2-10; R <sup>1</sup> , R <sup>2</sup> = optionally substituted hydrocarbon groups such as silicone, linear or branched alkyl, aryl, alkylaryl, aralkyl or cycloaliphatic groups (optionally unsaturated and/or with hetero-atoms); n = 1 or more, preferably 1-100 An <b>INDEPENDENT CLAIM</b> is also included for articles obtained by forming TPC, preferably by moulding, compression moulding, injection blow moulding, extrusion blow moulding, extrusion or spinning.
<b>NOVELTY</b> Functionalised, hyper-branched copolyamides are used as rheology modifiers in thermoplastic polymer compositions.  <b>DETAILED DESCRIPTION</b> A thermoplastic polymer composition (TPC) comprising a thermoplastic polymer-based matrix (M) and rheology-modifying additive(s) (PAHB) consisting of functionalised, hyperbranched copolyamide(s) obtained by reaction of (a) monomer(s) of formula A-R-B <sub>f</sub> (I), possibly (b) difunctional spacer monomer(s) of formula A'-R'-B' (II) or the corresponding lactams, possibly (c) core monomer(s) of formula R <sup>1</sup> (B) <sub>n</sub> (III) and (d) chain-regulating monomer(s) of formula R <sup>2</sup> -A (IV), at least 50% of the terminal groups in the copolyamide being functionalised by R <sup>2</sup> .	<b>USE</b> Functionalised hyperbranched copolyamides (as described) are used as rheology modifiers for thermoplastic polymer matrices (claimed). Polymers modified with these copolyamides are used e.g. for the production of moulded articles, yarn, fibres, film and filaments.  FR 2833603-A+

## ADVANTAGE

Functionalised hyperbranched copolyamides enable the controlled modification of the rheological properties of thermoplastics (especially melt viscosity) without adverse effects on mechanical properties such as impact strength and without changing the chemical structure of the matrix or reducing its mol. wt. These copolyamides are also readily dispersible in the matrix polymer.

## EXAMPLE

A preheated (70°C) reactor was charged in succession with 1867.4 g hexadecylamine (melt, purity 90%), 525.5 g ε-caprolactam, 840.6 g 5-amino-isophthalic acid, 162.5 g benzene-1,3,5-tricarboxylic acid and 6.1 g 50% aqueous hypophosphorous acid, then the mixture was stirred at 260°C for 30 minutes and vacuum was applied progressively over 1 hour, to give 2946 g hyperbranched copolyamide (PAHB-C16/2) and 155.2 g distillate. The product showed mol. wts. of 4890, 7750 and 11440 (Mn, Mw, Mz), a mol. wt. ratio of 1.58, an amine end group content of 3.1 meq/kg and an acid end group content of 7.7 meq/kg. A mixture of polyamide 6,6/50% glass fibres and 2 wt% PAHB-C16/2 showed a melt viscosity (flow spiral, 300°C) of 430 (339) mm and a

moisture content (before moulding) of 0.26 (0.20) %.

Injection moulded test samples showed a mol. wt. (PA 6,6) of 63550 (65250), an impact strength (un-notched) of 76.3 (82.4) kJ/m<sup>2</sup>, an impact strength (notched) of 10.3 (11.0) kJ/m<sup>2</sup>, a flexural modulus of 11500 (11800) N/mm<sup>2</sup>, a flexural strength of 262 (280) N/mm<sup>2</sup> and a heat distortion point of 245 (248) °C. Values in brackets are for unmodified PA66/50% glass fibres; the change in mol. wt. caused by the modifier was -2.6%.

Other combinations of melt viscosity and other properties were obtained by using different types and amounts of copolyamide modifier.

## DEFINITIONS

Preferred Definitions:

R, R' = linear or branched aliphatic groups and/or cycloaliphatic groups and/or mono- or poly-nuclear aromatic groups and/or aryl-aliphatic groups (all optionally substituted and/or containing hetero-atoms), with aromatic groups especially preferred for R in formula (I);

A, A' = amino, amine salt, acid, ester, acid halide or amide groups, preferably carboxylic or amino functions, with amino

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<p>especially preferred for A in (I); B, B' = acid, ester, acid halide, amide, amino or amine salt groups, preferably carboxylic or amino functions, with carboxylic especially preferred for B in (I);  f = 2</p> <p><b>TECHNOLOGY FOCUS</b>          Polymers - Preferred Compositions: Compositions containing no PAHB additives which cause a reduction of 7% or more in the mol. wt. of the matrix (M) (using a specified method for mol. wt. determination, preferably carried out on the composition to be analysed and the reference composition, both extruded, solidified and granulated and possibly subjected to a quantitative fluidity test (Qf)). Preferred compositions: The composition contains 0.1-50 (preferably 1-20, especially 2-10) wt% PAHB. Other components include reinforcing materials and/or fillers such as glass, aramid, ceramic or carbon fibres, mineral fillers, fillers based on thermosets and powdered fillers such as talcum. Preferred Copolyamides: Hyperbranched copolyamides (PAHB) with an acid or amine end-group content of 0-25 meq/kg, containing monomers (III) with a mol</p>	<p>ratio of (III)/(I+II+IV) = not more than 1/150, preferably not more than 1/100, especially not more than 1/50.          Preferred Matrix Polymers: Twenty-two polymer types listed, including e.g. polyolefins, polyesters, polyalkylene oxides, polyphenylene, polyvinyl acetates, polyvinyl halides, polyamides, polycarbonates, acrylic polymers, cellulose or its derivatives and thermoplastic copolymers.          Preferred polymers are (co)polyamides such as polyamide (PA) 6, 6,6, 4, 11, 12, 4-6, 6-10, 6-12, 6-36 and/or 12-12, especially PA 6 with a relative viscosity (1% in sulfuric acid at 25°C) of more than 3.5, preferably more than 3.8, or PA 6,6.          Preferred Articles: Moulded products, yarn, fibres, film or filaments obtained from TPC.          Organic Chemistry - Preferred Monomers: Monomer (I) comprises 5-amino-isophthalic, 6-amino-undecanoic, 3-aminopimelic, aspartic, 3,5-diaminobenzoic and/or 3,4-diaminobenzoic acid;          (II) comprises ε-caprolactam and/or aminocaproic acid, p- or m-aminobenzoic acid, 11-amino-undecanoic acid, lauryl-lactam and/or the corresponding amino-acid and/or 12-aminododecanoic acid;</p> <p>FR 2833603-A+2</p>

(III) comprises 1,3,5-benzenetricarboxylic acid, 2,2,6,6-tetra-( $\beta$ -carboxyethyl)-cyclohexanone, 2,4,6-tri-(aminocaproic acid)-1,3,5-triazine and/or 4-aminoethyl-octane-1,8-diamine;  
(IV) comprises n-hexadecylamine, n-octadecylamine, n-dodecylamine and/or benzylamine.  
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